

# **Transport, Cycling, and Fate of Mercury and Monomethyl Mercury in the San Francisco Delta and Tributaries: An Integrated Mass Balance Assessment Approach**

## **Introduction**

### ***Background***

There is widespread mercury contamination in fish, sediment and water in the Central Valley and Bay-Delta Estuary. This mercury poses a human health risk principally through the consumption of mercury-contaminated fish. Health advisories and interim health advisories have been posted in the Bay-Delta Estuary recommending no consumption of large striped bass and limited consumption of other sport fish. Elevated concentrations of mercury in fish tissue may also represent a hazard to piscivorous wildlife. Species most at risk are fish-eating birds and mammals. Mercury contamination in aquatic organisms results from the conversion of inorganic mercury (Hg) to monomethyl mercury (MMHg), principally by sulfate-reducing bacteria in surficial sediments. A recent study by the U.S. Geological Survey in twenty basins across the U.S. demonstrated a strong positive correlation between aqueous MMHg concentrations and fish tissue levels (personal communication, Krabbenhoft et al. (1999)). Therefore, an understanding of the sources and sinks of aqueous Hg and MMHg is essential both for the development of control programs to reduce fish tissue levels and also to ensure that CALFED wetland restoration efforts do not exacerbate an already serious human and wildlife health problem.

### ***Project Description and Objectives***

The work being described in this report represents the second phase of mercury investigations in the Bay-Delta Estuary by a team of principle investigators from Moss Landing Marine Laboratory (Mark Stephenson and Dr. Kenneth Coale), the Central Valley Regional Water Quality Control Board (Dr. Chris Foe) and Battelle Marine Sciences Laboratory (Dr. Gary Gill)<sup>1</sup>. The primary goal of this project is to provide an integrated research project on sources and loads of mercury in the Bay

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<sup>1</sup> Dr. Gill began this project while he was a faculty member at *Texas A&M University at Galveston*. Dr. Gill moved to *Battelle Marine Sciences Laboratory* in September 2005 and completed the project while at Battelle.

Delta watershed, and the transport, cycling and transformation that occur to mercury and MMHg within the watershed. This research project was designed to evaluate mercury sources and sinks and biogeochemical cycling using a mass balance approach. This research program seeks to expand upon previous findings to:

1. Fill in data gaps in our current conceptual understanding of Hg and MMHg sources, sinks, and cycling in the Bay-Delta and its watershed;
2. Verify and quantify seasonal variations of MMHg in sediments and in the water column with respect to habitat type;
3. Accurately characterize the spatial distribution of total Hg and MMHg in the Delta;
4. Estimate the loadings of MMHg from wetlands and evaluate their importance relative to other sources;
5. Provide a foundation and framework for long term monitoring of Hg contamination issues in the Delta.

### ***Current Working Hypotheses and Investigative Approaches.***

The work described in this study is based upon findings obtained in previous CALFED Mercury studies. The work to characterize the major reservoir concentrations and flows of Hg and MMHg in the Delta to date has lead to the development of the following working hypotheses. Also provided is a brief description of the proposed investigative approaches.

- 1. Riverborne MMHg is a major source of MMHg introduced to the Delta, especially under high river flow conditions.** This study will continue to conduct monitoring of the major riverine inputs and water export losses to the Delta on a seasonal basis for multiple years in order to address concerns regarding temporal variability.
- 2. Atmospheric Hg deposition is a minor, but significant source of total Hg loading to the Delta.** This study will set up a series of three (3) atmospheric deposition monitoring stations in key regions around the Bay, Delta, and associated watersheds to characterize the atmospheric deposition flows of Hg and MMHg into the Delta for both wet deposition and dry deposition.
- 3. Methylmercury concentrations in Delta sediments increase during late spring through early summer as a result of increased Hg methylation in the sediment.** This study will include monthly sediment

sampling in the Delta at four locations for three (3) years and increase the frequency of sampling from monthly to bi-monthly during late spring and summer.

- 4. Mercury and MMHg concentrations in Delta sediments are spatially variable relative to habitat type and the distribution remains relatively constant year to year.** This study will include sampling of twenty eight (28) locations, representative of the multiple habitat types found in the Delta. Sampling will occur twice a year (high flow season and low flow season) for two (2) years.
- 5. Within the Delta, wetland and marsh regions are major sites of MMHg production and enhanced sediment-water exchange flux.** This study will include a series of investigative studies to assess the importance of wetland or marsh habitats as sources of MMHg to the Delta. Investigative approaches include: benthic flux chamber deployments at marsh sites, monitoring of inflow and outflow Hg and MMHg concentrations to a marsh over a tidal cycle, and benthic sediment biogeochemical studies to try and understand controlling variables in surface sediments.
- 6. MMHg is lost from the water column within the Delta ecosystem by an unknown removal mechanism as water flows from the Sacramento River to the Delta.** This study includes a series of synoptic Delta transects to examine MMHg concentrations along water transport pathways. This information will be used as input to a hydrodynamic model of water flow in the Delta to investigate where MMHg is being lost (non-conservatively) and to quantify the magnitude of the loss.

### **Investigative Approach: A Mass Balance Geochemical Framework.**

The relative significance of all Hg and MMHg sources, sinks and cycling processes will be evaluated and constrained using a mass balance geochemical cycling framework, which is based on our conceptual understand of Hg transport and cycling behavior in the Delta and its tributaries. The geochemical processes quantified as part of this study will be used to inform a numerical model of solute transport so that quantitative budgets of Hg cycling can be produced.

### ***Task 1 – Project Management and Adminsitration***

All management and administrative subtasks have been completed.

## ***Task 2 – Mass Loading, Riverine Characterization and Export Studies***

Previous CALFED sponsored Hg studies have demonstrated the importance of river inputs in controlling Hg loads and aqueous and biotic concentrations in the Bay-Delta estuary. Multi-year loading studies are critical for understanding Hg processes and cycling in the system and for developing control programs to minimize the Hg hazard for people and wildlife.

### **Task 2.1 – Determine Mass loading estimates for Hg and MMHg into, and freshwater export from, the Delta**

Raw and filtered aqueous total and MMHg concentrations were determined monthly (filtered was determined at all stations twice per year only) at all the major inputs to the Bay-Delta (Sacramento, San Joaquin, and Mokelumne Rivers and Prospect Slough in the Yolo Bypass) and at the major export sites (State and Federal pumps and Chipps Island to estimate exports to San Francisco Bay). These measurements were coupled with flow estimates to calculate Hg loads and sinks (kilograms Hg/month).

### **Task 2.2 – Characterize tributary and regional input sources of MMHg and Hg in the Sacramento and San Joaquin Basins**

The primary goal of the river monitoring was to calculate mass balance estimates for raw and filtered total and MMHg for each river section (filtered samples will be determined twice per year only). Monthly river flow and Hg concentration data were collected at key locations down the Sacramento and San Joaquin Rivers and from all the major tributary inputs. This information was used to determine river reaches responsible for the major sources and sinks of Hg.

## ***Task 3 – Atmospheric Mercury Deposition Studies***

Work conducted under this task was designed to characterize the flux of atmospheric mercury deposition. Field work involved two major work efforts: (1) collection of atmospheric mercury wet deposition samples and (2) Determination of atmospheric mercury species (total gaseous mercury, TGM; reactive gaseous mercury, RGM; and particulate mercury, Hg<sub>p</sub>). The atmospheric mercury speciation measurements were used in modeling efforts to provide estimates of the dry deposition of mercury.

## ***Task 4 – Delta Wide Monitoring and Characterization Program***

### **Task 4.1 Determine Hg and MMHg in surface sediments of different Delta ecosystems (i.e. habitat-based)**

### **Task 4.2 – Benthic Flux Chamber Studies**

Sediment-water exchange studies were a major aspect of the first phase of our work and were also a major focus of this current study. In the first phase we focused on open water areas and in this current project we focused on near shore wetland areas.

## ***Task 5 – Process Oriented Studies***

A series of process-oriented studies were included in this research project to identify links between Hg and MMHg production and destruction and to derive environmental rate dependencies with respect to major biogeochemical processes and constituent concentrations.

### **Task 5.1 – Monomethyl Mercury Photo Demethylation Studies**

A recent study in the Experimental Lakes Area (ELA) of northwestern Ontario, Canada observed that MMHg in the water column can undergo destruction through a photodegradation process. If photodemethylation of MMHg is occurring in the Delta, this process could easily be the mechanism for the loss of MMHg that we have hypothesized occurs within the Delta as water flows from the Sacramento River to the export pumps in the southern portion of the Delta. To investigate the possibility that photodemethylation is the mechanism responsible for loss of MMHg in the Delta, this study included bottle incubation experiments during different seasons of the year at the sites where other process oriented tasks and intensive studies were being conducted.

### **Task 5.2 – Delta Transects and Cross Channel Studies**

Work conducted on the previous CALFED Mercury Project suggested that there is an internal sink for MMHg in the Delta. The objective of this task was to thoroughly document the existence of the sink and relate it to hydrologic, chemical, and biological parameters. The recently developed hydrologic forecast model developed by the DWR Delta Modeling Section provides a useful framework with which to test some of these assumptions and develop hypotheses.

### **Task 5.3 – Wetland Mass Loading and Sediment Biogeochemistry Studies**

The primary objective of the wetlands loading task was to determine loadings of MMHg from different types of wetland habitats and to compare the loadings from these wetlands to loadings from Delta tributaries, atmospheric deposition, and Delta sediment.

#### *Task 5.3a – MMHg Loading Studies in Delta Wetlands*

The objective of this task was to determine loadings of MMHg from different types of habitats (permanent tidal marshes, managed seasonal wetlands, permanent non-tidal wetlands, reference sites, and flooded tracts) and to compare the loadings from these wetlands to loadings from Delta tributaries, atmospheric deposition, and Delta sediment. Four locations were studied: Twitchell Island, Sycamore Slough and Suisun Marsh, Grizzly Island and Brown's Island. Using this approach, all the sources of MMHg can be put into perspective so their relative importance can be assessed.

#### *Task 5.3b – Sediment Biogeochemistry Studies in Delta Wetlands*

The primary site of MMHg production within an aquatic ecosystem usually occurs in near-surface anoxic sediments mediated by sulfate-reducing bacteria. Hence, there are a number of environmental variables, characteristics or conditions that could influence the net production of MMHg and its ultimate release into the water column. This task was designed to investigate the relationship between major biogeochemical processes in sediments and the production of MMHg. The field work for this task involved measurements of mercury and MMHg in interstitial pore waters using the whole-core squeezing technique and also high resolution near-surface profiles of oxygen, sulfide, and other parameters in interstitial pore waters using a microelectrode profiler system (Unisense).

### **Task 5.4 – Air-Water Exchange Studies of Dissolved Gaseous Mercury**

The formation of volatile Hg species, particularly elemental Hg, in surface waters, and evasion to the atmosphere is an important component of the cycling of Hg in aquatic systems. Moreover, Fitzgerald et al. (1994) has hypothesized that dissolved gaseous mercury (DGM) is an end product of the biotic de-methylation of MMHg. The air-water exchange of gaseous Hg species represents another data gap in our overall understanding of the cycling of Hg in the Delta. To the best of our knowledge, there have been no assessments of this process in the San Francisco Bay or Delta region to provide constraint of the cycling of Hg in these waters. This task was designed to address this data gap.

## **Task 6 – Integration of GIS into Program**

All data is in a GIS compatible format.

### **Quality Assurance, Quality Control**

The Quality Assurance Research Group of Moss Landing Marine Laboratories have completed 4 Intercomparison Studies that are presented in the Appendices of this report.

## **References**

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